# Enhancement of the advanced Fenton process (Fe$^0$/H$_2$O$_2$) by ultrasound for the mineralization of phenol

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## ARTICLE INFO

## ABSTRACT

In this study, a successful mineralization of phenol was achieved by means of coupling zero-valent iron (ZVI) particles, hydrogen peroxide and a short input of ultrasonic irradiation. This short sono-advanced Fenton process (AFP) provided a better performance of ZVI in a subsequent silent degradation stage, which involves neither extra cost of energy nor additional oxidant. The short input of ultrasound (US) irradiation enhanced the activity of the Fe$^0$/H$_2$O$_2$ system in terms of the total organic carbon (TOC) removal. Then, the TOC mineralization continued during the silent stage, even after the total consumption of hydrogen peroxide, reaching values of ca. 90% TOC conversions over 24 h. This remarkable activity is attributed to the capacity of the ZVI/iron oxide composite formed during the degradation for the generation of oxidizing radical species and to the formation of another reactive oxidant species, such as the ferryl ion. The modification of the initial conditions of the sono-AFP system such as the ultrasonic irradiation time and the hydrogen peroxide dosage, showed significant variations in terms of TOC mineralization for the ongoing silent degradation stage. An appropriate selection of operation conditions will lead to an economical and highly efficient technology with eventual large-scale commercial applications for the degradation organic pollutants in aqueous effluents.

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## 1. Introduction

Considerable efforts have been expended in treating industrial waters of various qualities in order to achieve stringent environmental regulations to make the wastewater suitable for consumption or discharge. Newer techniques are being developed to be used, mostly, in combination with conventional biological and chemical methods. Advanced oxidation processes (AOPs) have been found to be successful for the abatement of refractory and/or toxic organic pollutants in water and wastewater [1]. They are based on the generation of highly reactive hydroxyl radicals which have one unpaired electron and are exceptionally strong oxidizing agents. Among those processes, sonocatalysis is used for wastewater depuration. Sonochemical effects are largely attributed to the phenomena that results from cavitation which is the formation, growth and subsequent collapse of cavities releasing large quantities of energy locally, creating hot-spots and generating highly oxidizing hydroxyl radicals that provide the main driving mechanism for the degradation of pollutants. Indeed, ultrasonically induced cavitation has been used with great success for the

degradation of various pollutants, such as chlorinated hydrocarbons [2], aromatic compounds [3] or textile dyes [4] into short chain organic acids, carbon dioxide and inorganic ions as final products. However, the high operating costs of ultrasonic processes make this treatment a rarely used technique for cost-effective operations, due to the low degradation rates and mineralization degrees. In the case of reactions where the controlling mechanism is hydroxyl radical attack, sonocatalysis can be usefully combined with other oxidation agents such as ozone [5] or hydrogen peroxide [6] in order to enhance the rates of degradation due to additional generation of oxidizing radicals. The overall aim of the process is to mineralize the organic compounds completely, or at least partially, converting the initial compounds into less harmful products to allow direct discharge or make them more amenable to biological treatments. The effect of the combination of ultrasound with the Fenton reagent (Fe$^{2+}$/H$_2$O$_2$) has been also widely studied. However, the use of stoichiometric quantities of ferrous ions is a major drawback of the traditional Fenton process, and so alternatives such as zero-valent iron (Fe$^0$) have been successfully applied [7,8]. The advantage of using a heterogeneous system is the easy removal of the zero-valent iron (ZVI) by filtration. Moreover, ultrasonic irradiation generates benefits in heterogeneous systems by decreasing mass transfer limitations and fragmentation of the solid into small particles that provide a higher surface area [9]. Ultrasound is mostly a cost

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intensive operation and in published literature reporting those systems, the time of the treatment is a limiting factor in the overall cost. Treatments involving either ultrasound alone or a sonocatalytic system require 4–6 h sonication for sufficient degradation to be observed [10].

ZVI has also been applied due to effectiveness, low cost and benign environmental impact for the in situ remediation of groundwater. Over the last decade, several studies have demonstrated that ZVI effectively reduces the concentration of several organic and inorganic pollutants [11,12]. Under oxic conditions, the oxidation of $Fe^0$ to $Fe^{2+}$ is accompanied by the production of $H_2O_2$ from the reduction of $O_2$. The ensuing combination of $Fe^{2+}$ and $H_2O_2$ (known as the Fenton reagent) generates hydroxyl radicals upon the oxidation of ferrous ion by $H_2O_2$ [13]. Therefore, it has been shown that oxidative processes occur but the procedure seems to be of limited efficiency for degradation of contaminants because the yields of oxidants formed are usually low [14]. As a result, this approach is unlikely to be competitive with existing AOPs because less than 5% of the iron added is converted into oxidant species capable of degrading contaminants [13]. The efficiency of the oxidative ZVI system appears to improve in the presence of electron shuttling molecules, such as EDTA (ethylenediaminetetraacetic acid) [15] or POM (polyoxometalate) [14]. Also the addition of low concentrations of $H_2O_2$ can enhance the efficiency of organic compound removal [12]. It has been shown that the combination of ultrasound and ZVI is a good alternative to enhance the oxidative capacity of ZVI due to the synergistic mechanism obtained in the combined system [16–18]. However, degradation rates are still quite limited due to the low generation of hydrogen peroxide formed during corrosion.

The advanced Fenton process (AFP), which utilises ZVI, has been studied as a potential technique to degrade different pollutants in wastewater [19]. Moreover, Bremner et al. [20,21] have reported the degradation of organic compounds using ultrasound combined with the $Fe^0/H_2O_2$ system, although in these cases degradation had always been examined in the presence of excess hydrogen peroxide.

In this current work, the removal of phenol has been investigated by coupling zero valent iron and hydrogen peroxide (advanced Fenton process) with ultrasound. This approach is investigated in order to minimize the ultrasonic irradiation time and to moderate dosages of hydrogen peroxide. Only a few minutes of ultrasonic irradiation were applied instead of using the longer times of conventional reactions [10]. After the initial input of ultrasound, the degradation of the phenol is allowed to continue silently afterwards. This work is focused on studying the effect of different operating conditions of the sono-AFP with the goal of determining their influence in the degradation of an aqueous phenolic solution during the subsequent ongoing degradation. The effect of various reaction parameters, such as time of ultrasonic irradiation, concentration of oxidant, and presence or absence of ZVI has been assessed in this work.

## 2. Materials and methods

### 2.1. Regents

Phenol (Scharlab, 100% pure), iron metal powder (Sigma–Aldrich, 97% pure) and hydrogen peroxide (Scharlab, 30% pure) were used as purchased.

### 2.2. Experimental procedures

Sono-AFP reactions were performed with an ultrasonic Sonicator 3000 (Misonix), equipped with a titanium horn-probe (tip

diameter of 2 cm) working in a continuous mode at a fixed frequency of 20 kHz and a power output of ca. 90 W. In a typical experimental set-up, a cylindrical glass vessel was filled with 200 mL of an aqueous phenolic solution (2.5 mM equivalent to $(TOC)_0$ of 179.0 mg $L^{-1}$) and appropriate amounts of hydrogen peroxide. The temperature was controlled at $22 \pm 2\,°C$ during the ultrasonic irradiation to avoid any overheating of the aqueous solution and was then maintained at room temperature (ca. 22 °C) for the subsequent step of silent degradation. The iron metal was suspended in the aqueous solution (0.6 g $L^{-1}$) and gently mixed using a magnetic stirrer while adjusting the pH to ca. 3 with $H_2SO_4$ (0.1 M) and then left undisturbed in the dark throughout the reaction time, unless otherwise specified. The initial concentration of hydrogen peroxide was either half the stoichiometric amount (595 mg $L^{-1}$), the stoichiometric amount (1190 mg $L^{-1}$) or twice the stoichiometric amount (2380 mg $L^{-1}$) (coded as 50%, 100% and 200%, respectively) for the theoretical complete mineralization of phenol to $CO_2$ and $H_2O$.

The reaction mixture was then irradiated with ultrasound for 1, 5 or 10 min prior to being left silently at RT in the dark for up to 24 h. Samples were taken at 0, 1, 3, 5 and 24 h, where 0 means the end of US irradiation (after 1, 5 or 10 min) and the beginning of silent degradation.

Aliquots (ca. 20 mL) were withdrawn throughout the reaction time and filtered through 0.22 μm nylon membranes prior to analysis. Total organic carbon (TOC) content of the samples was determined using a combustion/non dispersive infrared gas analyzer model TOC-V (Shimadzu). Hydrogen peroxide concentration was measured by iodometric titration and the iron content in the filtered solution after reaction was measured by ICP-AES analysis using a Varian Vista AX spectrometer. The pH of the solution was measured using a Metrohm pH meter.

### 2.3. Characterization of the ZVI samples

In order to characterize the ZVI before and after the treatments, several techniques were used. X-ray powder diffraction (XRD) recorded in the $2\theta$ range from $10°$ to $70°$ were obtained with a Philips X-Pert diffractometer using Cu Kα radiation.

Temperature programmed reduction (TPR) was performed in a Micromeritics Autochem 2910 instrument. The sample was heated from 323 to 1173 K (heating rate 10 K/min) under a hydrogen–argon mixture (10% $H_2$) with a flow rate of 40 mL/min. Specific surface areas of samples were calculated from nitrogen sorption isotherms at 77 K using a Micromeritics Tristar 3000 system.

## 3. Results and discussion

### 3.1. The effect of ultrasound and the ZVI on the oxidative degradation of phenol

In order to evaluate the effect of sonication (5 min) as a pretreatment to accelerate the activity of the ZVI during the silent degradation of phenol, different experiments were carried out using the same operating conditions but: (i) in the absence of hydrogen peroxide ($US + Fe^0$), (ii) in the absence of ZVI ($US + H_2O_2$) and (iii) stirring instead of ultrasound ($ST + Fe^0 + H_2O_2$). Fig. 1 illustrates the TOC, pH, $H_2O_2$ and iron dissolution profiles of those different experiments compared to values for 5 min sonication and subsequent 24 h of silent degradation in presence of the ZVI.

The results of the experiment in the absence of hydrogen peroxide ($US + Fe^0$) showed no TOC degradation, and the pH remained virtually constant at 2.5 over the 24 h. The amount of iron dissolved in this experiment increased immediately after the sonication step
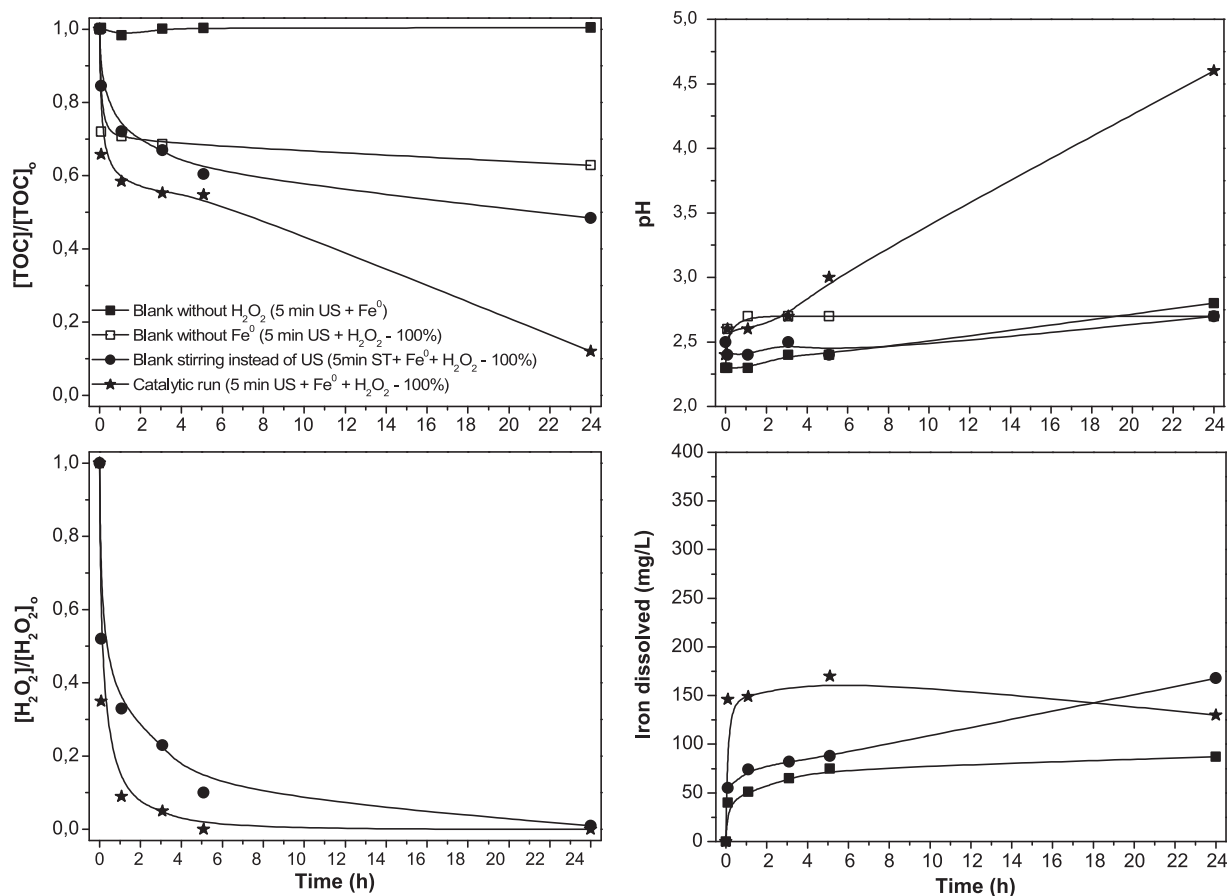
**Fig. 1.** Influence of the initial reaction conditions on phenol degradation in terms of TOC removal, pH, $H_2O_2$ concentration and iron concentration in solution.

followed by a slight increase over time, achieving a maximum value of 80 mg L$^{-1}$ after 24 h. In the absence of ZVI (US + $H_2O_2$), the TOC conversion was only 30% after 5 min of ultrasound irradiation and showed no further TOC reduction over the following 24 h.

These results evidence a low activity of the ZVI in the absence of the oxidant. Note that the presence of dissolved oxygen in the solution is considered one of the primary requirements for a successful application of ZVI particles [22]. As this experiment was carried out under an air-atmosphere but not in saturated-oxygen water, the mineralization of phenol was not observed in the absence of initial hydrogen peroxide. In contrast, the presence of the oxidant without ZVI yielded a significant TOC reduction when ultrasound was applied, but a negligible impact in silent conditions.

The combination of ZVI and oxidant (US + Fe$^0$ + $H_2O_2$) showed some increase of the TOC mineralization during the 5 min of reaction, but was especially noteworthy during the silent degradation stage, achieving almost 90% after 24 h. It must be also pointed out that most of the TOC mineralization took place throughout the silent degradation step when the hydrogen peroxide was depleted after 5 h. With regard to the iron dissolved into the solution, a maximum value of ca. 150 mg L$^{-1}$ was measured immediately after the ultrasound process, remaining constant then throughout 24 h. The pH also increased during the US + Fe$^0$ + $H_2O_2$ process, giving a value of ca. 4.5 after 24 h.

The effect of the initial input of ultrasound on the performance of the silent oxidation step was compared to the experiment using stirring (ST + Fe$^0$ + $H_2O_2$) instead of ultrasound (US + Fe$^0$ + $H_2O_2$) during 5 min of treatment. Stirring yielded much lower TOC removal after 5 min and also after the following 24 h. In contrast to the experiment using 5 min of ultrasound, the pH did not drastically change during the process. The dissolution of iron was initially

lower but increased throughout the silent degradation stage up to concentrations similar to those obtained for the US + Fe$^0$ + $H_2O_2$ experiments. In the case of using ultrasound, the profile of dissolved iron can be probably related to the change of the pH throughout the silent remediation, producing the iron precipitation as the pH increases. In fact, the level of dissolved iron after 24 h was even lower than that obtained by the blank experiment using stirring.

In order to evaluate the effect of the ZVI during the degradation of phenol, an additional experiment was carried out when the ZVI was filtered off after 5 min of ultrasound irradiation in the presence of $H_2O_2$ (100%). The ensuing ongoing degradation process was then carried out in absence of the ZVI under silent conditions. The result of this experiment was compared to the same experiment but maintaining the ZVI throughout the silent degradation stage. In both cases, the samples were analysed in terms of TOC conversion over 1, 3 and 24 h (Fig. 2).

The results obtained reveal the great influence of ZVI in the silent degradation process. In the experiment where the iron was filtered off after the initial ultrasound input, the TOC mineralization hardly continued with only a minor increase of less than 10% over the following 24 h. In contrast, in the presence of the ZVI the TOC removal increased by more than 50%. Also noteworthy is that the initial sono-advanced Fenton process enhanced the dissolution of iron species into the aqueous solution (approximately 150 mg L$^{-1}$), and which remained present up to 24 h. The low TOC conversion of the process when the Fe$^0$ was filtered off indicated that the contribution of homogeneous iron species can be ruled out. As previously mentioned, the remarkable TOC conversion during the silent degradation period was achieved in absence of hydrogen peroxide, as the oxidant was completely depleted in the first 3 h. This fact clearly
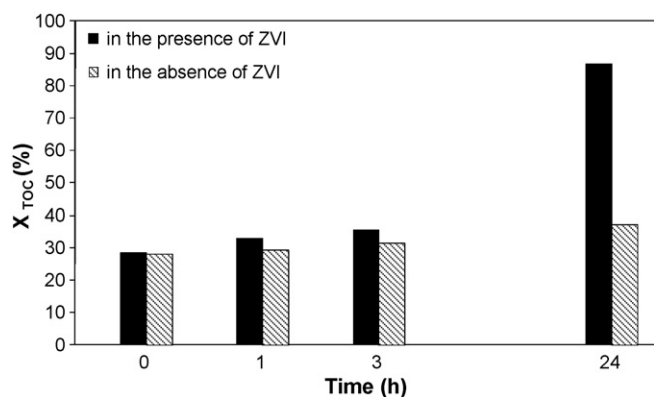
**Fig. 2.** Effect of ZVI on the phenol degradation in terms of TOC conversion for the silent degradation process. Initial sono-AFP conditions: 5 min of US and 100% of $H_2O_2$.

suggests that the ZVI plays a key role in the continuing TOC mineralization during the silent degradation.

### 3.2. The effect of the initial $H_2O_2$ concentration and time of ultrasound irradiation on the oxidative degradation of phenol

As discussed above, the initial application of ultrasound for only 5 min improved the extent of mineralization of phenol in the presence of ZVI for the following silent degradation step. For this reason, the effect of the initial ultrasound irradiation time (1, 5 and 10 min) using different concentrations of $H_2O_2$ (50, 100 and 200% of the stoichiometric amount) on the continuous degradation of phenol was also studied. The results of the TOC conversion for the different experiments are shown in Fig. 3.

The increase of the hydrogen peroxide concentration showed a clear enhancement of performance of the ZVI for all the ultrasound irradiation times evaluated during the sonication step. In this sense, the results of TOC conversion at zero time, which correspond to 1, 5 and 10 min of ultrasound were in the range of 9–15%, 30–45% and 30–60% for the series of experiments carried out at 50, 100 and 200% of $H_2O_2$ concentration, respectively. It can be seen that these TOC conversion ranges increased as the concentration of hydrogen peroxide rises, which indicated the relevant role of the oxidant. On the other hand, for the same initial hydrogen peroxide concentration, the increase of the ultrasound irradiation time led also to an increase of TOC degradations, except in the case of 50% where small differences were observed. The TOC mineralization for 1, 5 and 10 min of ultrasound achieved 29, 35 and 44% using 100% $H_2O_2$ and 28, 50 and 62% using 200% $H_2O_2$.

After the initial input of ultrasound (1, 5 or 10 min using 50, 100 or 200% of $H_2O_2$), the TOC concentration was also monitored for 24 h of silent degradation (Fig. 3). From these results, it was seen that the TOC mineralization continued after the initial sono-AFP. However, this increase seemed to be dependent on the ultrasound irradiation time and the $H_2O_2$ concentration used during the initial sono-AFP. For the lower hydrogen peroxide concentration (50%), the TOC conversion remained almost constant, irrespective of the ultrasound irradiation time applied. In the case of 100% of $H_2O_2$, there was a gradual increase during the first 3 h and then a significant rise over the 24 h. It is important to note that this performance under silent conditions was achieved in the absence of hydrogen peroxide, as $H_2O_2$ was completely consumed after 3 h. When 200% of hydrogen peroxide was used, the TOC conversion increased during the first hour until values of 50–60% for all the three ultrasound irradiation times and stayed almost constant over the full silent degradation time. These results indicate that with only 5 min of ultrasound input and 100% of hydrogen peroxide ca. 90% TOC
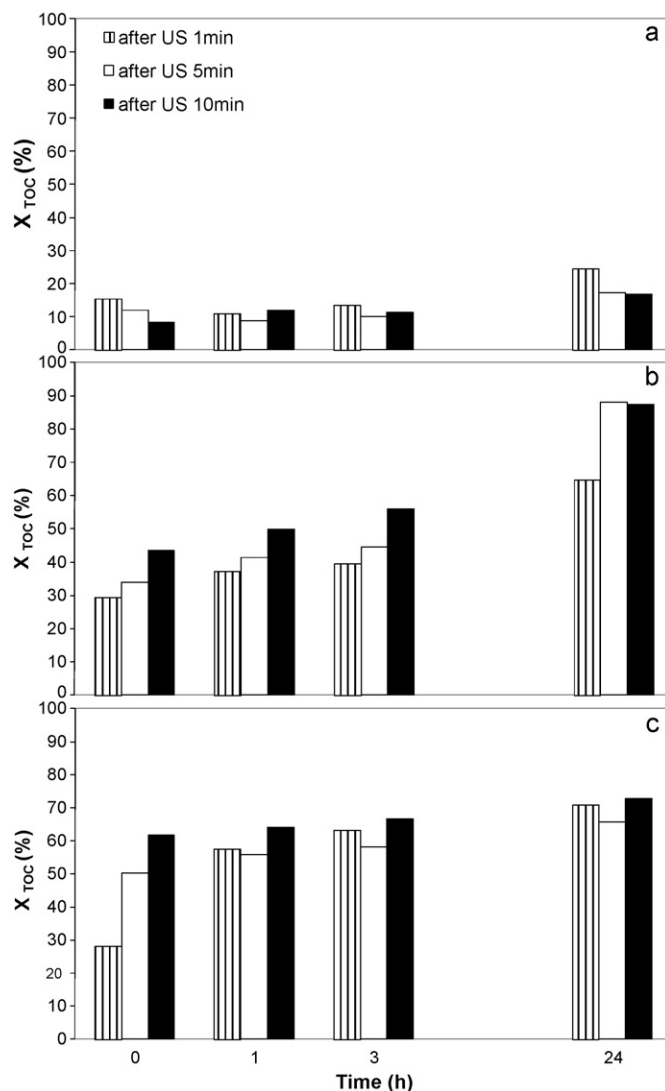


**Fig. 3.** Comparison of TOC degradation over time using different US irradiation times (1, 5 or 10 min) and hydrogen peroxide concentrations (a) 50%, (b) 100% or (c) 200%.

conversion was observed under silent degradation conditions. This indicates a huge reduction in cost saving can be obtained using this process.

### 3.3. Characterization of the ZVI powder during the silent degradation period

In order to gain some insight into the mechanism of the reaction, the surface of the ZVI was examined over time using X-ray diffraction. Fig. 4 shows the XRD patterns of fresh and used ZVI samples after the sono-AFP ($US + Fe^0 + H_2O_2$) and the following 24 h of silent degradation. The $US + Fe^0 + H_2O_2$ sample after 5 min of US showed similar XRD patterns as that of fresh $Fe^0$, which is readily indexed as a cubic phase (Fig. 4), showing no iron oxide in a crystalline phase. After 24 h, though the characteristic peaks of $Fe^0$ are still present, the appearance of a new weak signal at 18.30 assigned to magnetite ($Fe_3O_4$) demonstrated the formation of iron oxide entities. The presence of other iron oxide phases cannot be ruled out from these results, but their small particle size makes their identification by XRD very difficult. Therefore, temperature programmed reduction (TPR) analyses were carried out on the fresh and used ZVI after 24 h of silent degradation (Fig. 5). As expected, the TPR profile of fresh ZVI did not show any reduction peak. However,
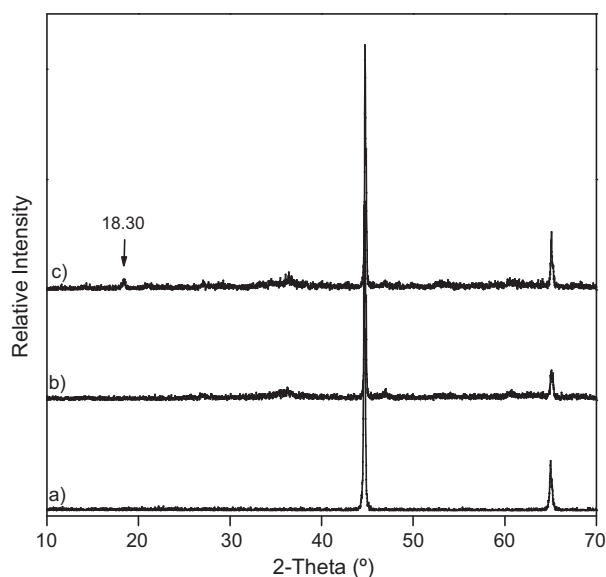
**Fig. 4.** XRD patterns of (a) fresh ZVI and (b) ZVI after sono-AFP reaction using 5 min of ultrasound irradiation (100% $H_2O_2$) and (c) after 24 h of silent degradation.

the ZVI after 24 h showed an intense reduction peak which confirmed the presence of magnetite ($Fe_3O_4$) centred at 450 °C but also other iron oxide phases such as wüstite (FeO) at 550 °C and probably goethite at 300 °C. Therefore, the presence of magnetite as previously attested from the XRD results was confirmed by TPR analyses, indicating that the metal iron surface was being covered by iron oxides during the silent degradation stage. These data are in agreement with those reported in the literature for the application of ZVI particles in aerated water systems [11].

Also, the BET surface area of the fresh ZVI changed from ca. 5 to 53 $m^2/g$ after 5 min of US and decreased to 39 $m^2/g$ after 24 h of silent degradation. The initial increase of surface area after the application of ultrasound is attributed to the well-known benefits of ultrasound for the fragmentation of solids, and therefore increasing its surface area. The data from TPR and the decrease of surface area of ZVI sample after the silent degradation is in agreement with the results reported by Moura et al. [23] who observed that the production of the wüstite phase under certain experimental conditions led to a decrease in BET surface area and reactivity.
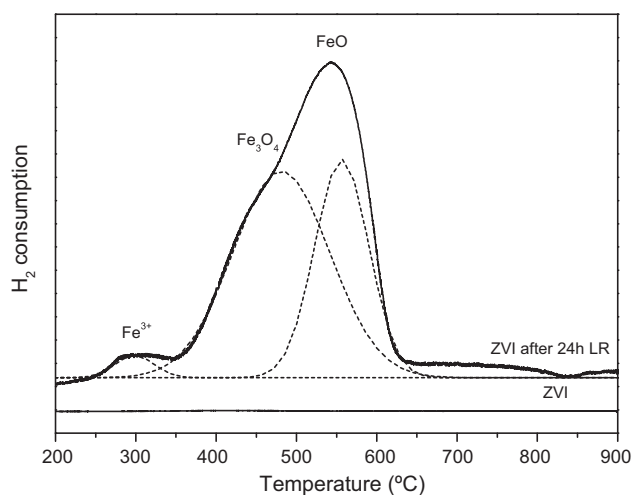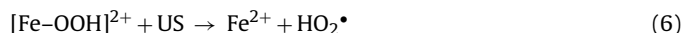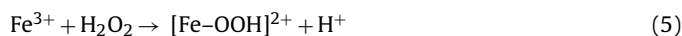


**Fig. 5.** TPR profiles of fresh ZVI and used (5 min US-AFP) ZVI after 24 h of silent degradation.

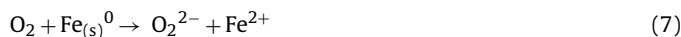### 3.4. Silent degradation of ZVI systems activated by ultrasonic irradiation

The mineralization of phenol involves the oxidation of the organic matter by the generation of hydroxyl radicals. The presence of solid particles under ultrasonic irradiation increases the cavitation nuclei due to the discontinuity of the liquid medium and increases also the cavitation effect for the production of hydroxyl radicals by the dissociation of water (Eq. (1)). Likewise, the ultrasonic irradiation also enhances the cleavage of hydrogen peroxide into hydroxyl radicals (Eq. (2)). The use of ZVI in the presence of hydrogen peroxide under acidic conditions and ultrasonic irradiation, leads to the corrosion of the iron metal, producing soluble ferrous ions (Eq. (3)). The $Fe^{2+}$ produced, is able to react with $H_2O_2$ in a Fenton-like process to generate hydroxyl radicals and $Fe^{3+}$ (Eq. (4)) [24]. The regeneration of $Fe^{2+}$ by the reduction of $Fe^{3+}$ to continue the cycle is enhanced by ultrasound, promoting the reduction of the $[Fe–OOH]^{2+}$ complex ion (Eqs. (5) and (6)). Therefore, the combination of ZVI in the presence of hydrogen peroxide in acidic conditions and ultrasound increases the production of oxidizing hydroxyl species. According to these reactions, the influence of the time of ultrasound and the initial hydrogen peroxide concentration on the TOC mineralization during the initial short period of ultrasound irradiation is in agreement with the benefits of those variables on the preliminary sono-AFP studies reported in literature [21].

$$H_2O + US \rightarrow HO^\bullet + H^\bullet \tag{1}$$

$$H_2O_2 + US \rightarrow 2HO^\bullet \tag{2}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow [Fe–OOH]^{2+} + H^+ \tag{5}$$

$$[Fe–OOH]^{2+} + US \rightarrow Fe^{2+} + HO_2^\bullet \tag{6}$$

The continuous TOC reduction during the silent degradation step after the ultrasonic treatment, revealed a latent activity of the ZVI in dark and silent conditions. It was also observed that the initial sono-Fenton conditions (irradiation time and initial hydrogen peroxide concentration) affected the ongoing degradation during the silent conditions. The influence of both variables is a complex process with an important role influencing the corrosion of ZVI. This corrosion will lead not only to the formation of ferrous ions, but also to the modification of the ZVI physicochemical properties by the generation of reactive iron species on the ZVI surface. The appearance of ferrous ions in the bulk liquid is specially favoured under acidic conditions and they promote the formation of hydroxyl radicals by typical Fenton reactions. Thus, this hypothesis could support the role of ZVI in terms of TOC mineralization during the silent stage, when the initial hydrogen peroxide was not completely consumed. However, the results shown in Fig. 2 indicated a significant decrease in TOC conversion when the ZVI, initially activated by the sono-advanced Fenton process, was removed from the aqueous solution. This reduced TOC mineralization rate in the absence of ZVI particles clearly evidenced the heterogeneous role of reactive iron species on the ZVI surface and therefore a low homogeneous contribution of the dissolved iron.

It was noteworthy that the TOC decrease continued throughout the silent degradation, even after the hydrogen peroxide was totally consumed. Keenan and Sedlak in 2008 proposed different mechanisms in order to support the activity of ZVI particles under aerated conditions with no initial addition of hydrogen peroxide [13,14]. These mechanisms were based on the formation of reactive oxygen species (ROS) capable of oxidizing contaminants such as recalcitrant organic compounds, chlorinated compounds or EDTA. In these mechanisms, hydrogen peroxide can be formed from the

reaction of ZVI (Eqs. (7)–(9)) or the ferrous ions (Eqs. (10)–(12)) with oxygen under acidic conditions, which come from the decomposition of hydrogen peroxide according to Eq. (13). Then, once the hydrogen peroxide is formed, its heterogeneous decomposition over the ZVI particles via Fenton reactions could be occurring for the generation of hydroxyl radicals to oxidize the organic matter.

$$O_2 + Fe_{(s)}^0 \rightarrow O_2^{2-} + Fe^{2+} \tag{7}$$

$$O_2^{2-} + H^+ \rightarrow HO_2^- \tag{8}$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \tag{9}$$

$$O_2 + 2Fe^{2+} \rightarrow O_2^{2-} + 2Fe^{3+} \tag{10}$$

$$O_2^{2-} + H \rightarrow HO_2^- \tag{11}$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \tag{12}$$

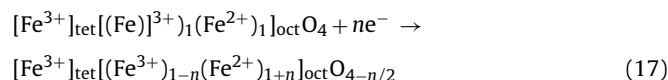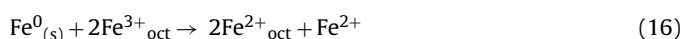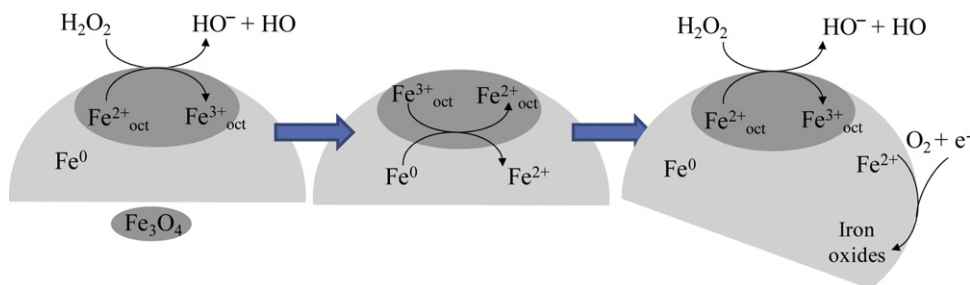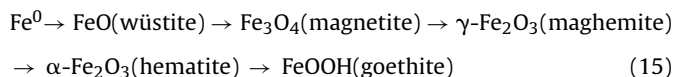$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{13}$$

The potential application of ZVI particles under acidic and aerated conditions has been reported for the mineralization of acetic acid, an example of a very recalcitrant pollutant (Eq. (14)) [25]. These results indicate that if acetic acid, can be effectively removed, other less stable pollutants like aromatic compounds will also be readily degraded, as it has been demonstrated herein for the mineralization of phenol and the formed by-products during the silent degradation.

$$Fe^0 + 8O_2 + 24H^+ + CH_3COOH \rightarrow 8Fe^{3+} + 2CO_2 + 14H_2O,$$

$$\Delta G^\circ = -3749.3 \tag{14}$$
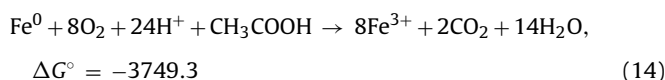
Regarding the heterogeneous catalytic activity of the ZVI particles, it must be pointed out the formation of ZVI/iron oxide mixtures on the particle surface following the Eq. (15).

The generation of hydroxyl radicals from magnetite and iron oxide particles as a heterogeneous system has been already reported [26]. Particularly, there are several reports on the decomposition of hydrogen peroxide by different ZVI/iron oxide composites prepared by mechanical grinding or thermal treatment [23,27]. The mixture of ZVI and magnetite ($Fe_3O_4$) showed strong activity towards hydrogen peroxide decomposition and methylene blue oxidation [28]. These results were attributed to the interaction of $Fe^0$ and $Fe_3O_4$, and suggested that $Fe_3O_4$ can aid the electron transfer from $Fe^0$ by acting as an intermediate/interface. In this mechanism, the electron is transferred from $Fe^0$ to $Fe^{3+}$ magnetite to produce or regenerate $Fe^{2+}$ magnetite (Eq. (16)) which is the active site for the Fenton reaction. This mechanism is supported by the octahedric sites of the magnetite spinel structure which are very versatile redox sites that can accommodate both $Fe^{3+}$ and $Fe^{2+}$ (Eq. (17)). Likewise, this process is thermodynamically favourable according to Eq. (16) ($\Delta E^0 = 1.21$ V).

$$Fe^0 \rightarrow FeO(\text{wüstite}) \rightarrow Fe_3O_4(\text{magnetite}) \rightarrow \gamma\text{-}Fe_2O_3(\text{maghemite})$$

$$\rightarrow \alpha\text{-}Fe_2O_3(\text{hematite}) \rightarrow FeOOH(\text{goethite}) \tag{15}$$

$$[Fe^{3+}]_{tet}[(Fe)]^{3+})_1(Fe^{2+})_1]_{oct}O_4 + ne^- \rightarrow$$

$$[Fe^{3+}]_{tet}[(Fe^{3+})_{1-n}(Fe^{2+})_{1+n}]_{oct}O_{4-n/2} \tag{17}$$

In this work, the presence of iron oxides on the surface of the ZVI particles throughout the silent degradation period was demonstrated by the XRD and TPR analysis. The initial conditions of the sono-advanced Fenton process played a crucial role, not only on the performance during the ultrasonic irradiation stage, but also during the ongoing degradation under silent conditions. Thus, 100% of $H_2O_2$ was shown to be the optimum oxidant concentration for the generation of reactive oxygen species achieving a suitable modification of the ZVI/iron oxide surface, mainly magnetite, throughout the 24 h of silent degradation. However, when using sono-AFP with lower (50%) and higher (200%) oxidant concentrations decreased TOC mineralization is observed. Concentrations of 50% of $H_2O_2$ might not be enough for the generation of reactive oxygen species. In the case of 200% of $H_2O_2$, the decrease in the overall performance during the silent degradation could be associated with a large build-up of iron oxides on the surface of ZVI that could eventually hinder the electron transfer process needed for a good interaction between ZVI and magnetite [29].

However, the continuous TOC reduction throughout the silent degradation, after the disappearance of the hydrogen peroxide, seems to indicate the presence of other oxidant species. It must be noted that under all experimental conditions carried out in this study, the reactions tended towards neutral pH values as the oxidation proceeded. Although, the nature of the oxidants involved when $Fe^{2+}$ reacts with $H_2O_2$ at circum-neutral pH values is still a controversial issue [30], strong evidence suggests that an oxidant other than hydroxyl radicals is formed as the pH tends towards neutral values. Keenan and Sedlak [13] indicated that the nature of the oxidants formed in nanoparticulate ZVI systems depends on the pH of the solution, varying from hydroxyl radical at low pH to another reactive oxidant species (such as the ferryl ion) at around neutral pH values. Therefore, the oxidizing power of ferryl ions, as $[Fe^{IV}O]^{2+}$, could be contributing somewhat to the TOC decrease during the final silent degradation stage as a less reactive but more selective oxidant than OH radicals [31].

## 4. Conclusions

The activation of ZVI particles by a very short input of ultrasound and moderate dosages of hydrogen peroxide is considered an attractive alternative to enhance the activity of ZVI throughout the silent degradation step under low cost operating conditions. In this study, up to 90% of phenol mineralization was obtained after 24 h of silent degradation after applying only a few minutes of ultrasound at the outset. The remarkable results of TOC mineralization can be mainly attributed to the transformation of ZVI to ZVI/iron oxides. This composite is active as a result of the formation of reactive radical species on the ZVI/iron oxides interface. Additionally, the presence of ferryl ion complexes of high oxidative capacity, are



$$Fe^0_{(s)} + 2Fe^{3+}_{oct} \rightarrow 2Fe^{2+}_{oct} + Fe^{2+} \tag{16}$$

also contributing the continued mineralization of the remaining organic intermediates. The main advantages of this system are that no expensive catalysts, solvents, pH maintenance nor long-term external sources of energy are required.

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